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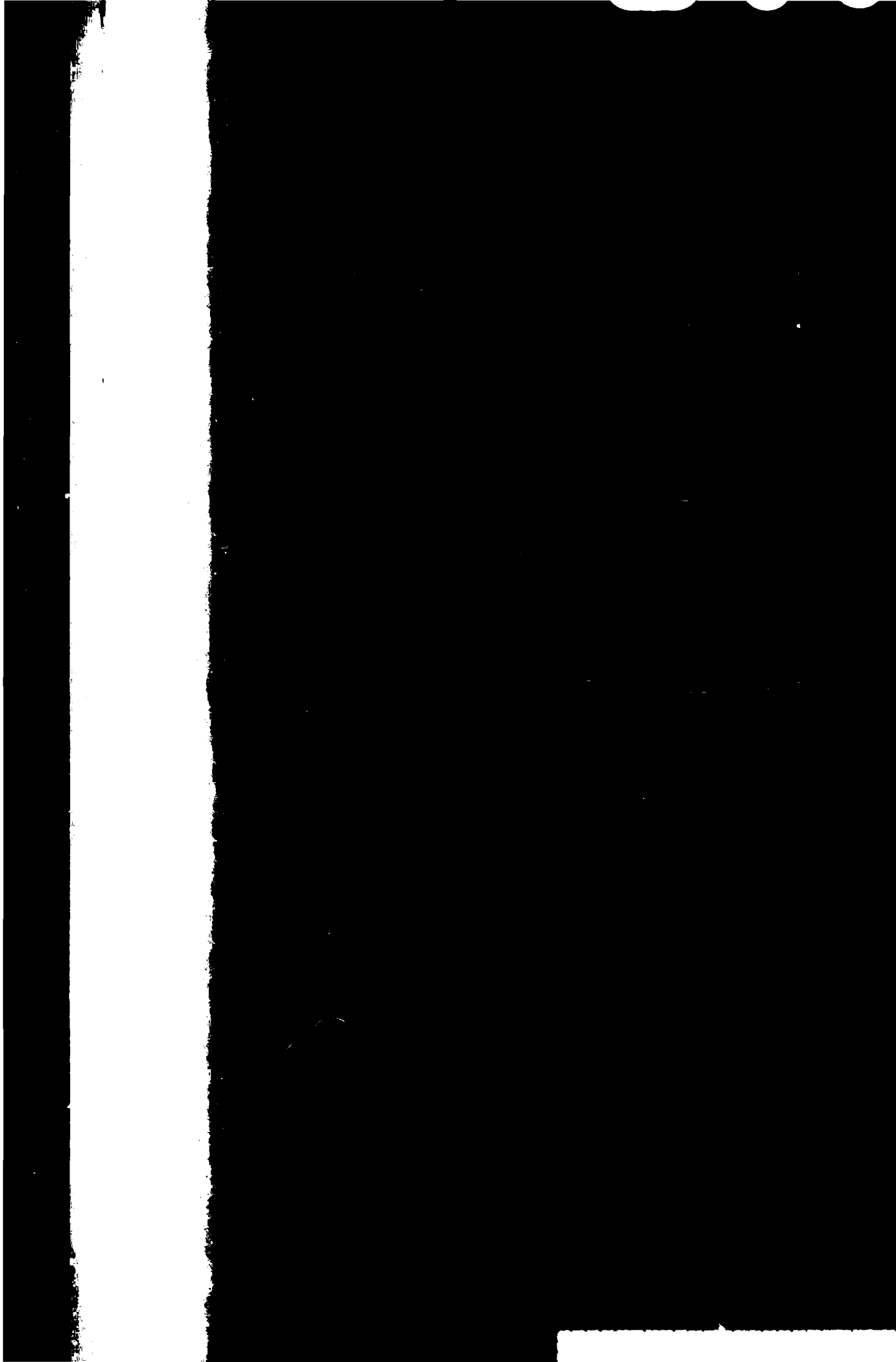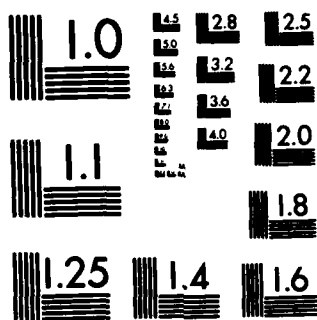MICROCOPY RESOLUTION TEST CHART
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SOLIDIFICATION OF HIGHLY UNDERCOOLED LIQUID DROPLETS

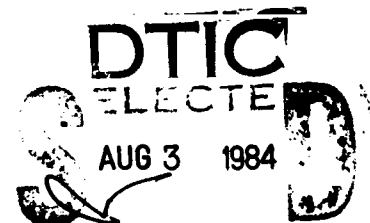FINAL REPORT
9/1/80 - 10/31/83

J. H. Perepezko

July 5, 1984

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The rapid solidification of highly undercooled liquid alloys in fine droplet form has been studied under controlled conditions by thermal analysis, x-ray diffraction and metallographic examination. Droplet undercooling is affected by processing variables such as particle size, melt superheat and cooling rate, but the undercooling limit is often set by a catalysis at the droplet surface. By varying the droplet coating and nucleation site the development of solidification microstructure and the effect of recalescence thermal history has been examined at controlled undercooling levels including the hypercooling range. In alloys

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some aspects of the phase selection kinetics and the effect of pressure on nucleation have been explored to identify solidification reaction pathways for metastable phase formation. The application of the droplet technique has been extended to high melting temperature Al alloys where substantial undercoolings in excess of 160°C can yield powder microstructures similar to those formed following air atomization.

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I. Introduction

During the period of project support from September 1, 1980 to October 31, 1983 research has been focussed upon phase selection reactions involved in metastable phase formation, evolution of solidification microstructure and other aspects of the undercooling and solidification of alloys. The experimental approach that has been applied to carry out these studies involves the droplet-emulsion technique. With this method samples may be produced which exhibit large undercoolings prior to solidification during slow cooling and which may be maintained in the metastable undercooled state for extended time periods without the intervention of crystallization.

For some alloys, the large undercoolings that are attained in droplets permit the liquid to bypass equilibrium crystallization and generate metastable solid phases. With these alloys it has been possible to examine the undercooling conditions for metastable phase formation and to elucidate the kinetic competition during crystallization. In certain other alloys attention has been directed towards the determination of the maximum undercooling to solidification and the reaction kinetics during important solidification reactions such as eutectic, peritectic and monotectic processes. Often the microstructural morphology and structure of product phases that solidify from the melt have features which are distinct to high undercooling solidification. Several examples of metastable phase formation, including vitrification, have been identified by thermal analysis and x-ray diffraction and a uniform microstructural morphology has been observed in some droplets indicating an absence of a heterogeneous dendritic crystallization.

For selected reactions it has been possible to identify the solidification path for crystallization from the undercooled liquid. With samples containing primary phase nucleation catalysts simultaneous thermal analysis and x-ray diffraction study has been used to identify a path for the generation of supersaturated solid solutions and metastable intermediate phases. In a complimentary examination the use droplet samples with controlled undercooling levels has permitted the documentation of morphological transitions from dendritic to plane front single phase growth and the analysis of microstructural evolution under the combined effects of undercooling and recalescence.

New applications and methods involving droplet samples have also been developed during the research period. Droplet samples have been examined in a high pressure thermal analysis apparatus. It has been discovered that only modest pressures (~ 1 kbar) are necessary to alter completely the product selection in highly undercooled droplets. The altered product phase selection is also reflected by a modified microstructural morphology. A modified droplet emulsion technique has been developed to permit the generation of droplet samples in high melting temperature aluminum alloys. With this approach rapid solidification has been examined in Al, Al-Fe and Al-Si samples. Not only have large undercoolings been achieved ($\Delta T > 160^{\nu}C$), but also droplet microstructures have been observed which are similar to those produced by rapid quenching treatment. As a result, droplet methods may be developed which can simulate the conditions involved in large scale commercial powder atomization treatments.

II. Droplet - Emulsion Technique

In order to achieve large undercooling levels, a liquid must not contain potent nucleants, nor can it be allowed to solidify in a container whose walls may catalyze nucleation.[1,2] As a result, large samples of liquid are generally unsuitable for obtaining maximum undercooling since they almost inevitably contain extraneous nucleants. Instead, the most promising method of attaining maximum undercooling during nucleation is to utilize a collection of small isolated droplets. By starting with high purity materials and dispersing the liquid metal into a large number of small droplets within a suitable carrier fluid only a few of the drops will contain potent nucleants. This is the principle of the droplet technique. If the droplets are maintained independent by films that are not nucleation catalysts, then the effects of any nucleants can be restricted to the few drops in which they are located. When a sample of liquid metal, in the form of an emulsion, is undercooled, the majority of the drops will not begin to solidify until the maximum undercooling temperature is reached. The growth rate of crystals from the liquid is very rapid at large undercooling. Hence, the formation of the first nucleus in any one drop will lead to rapid solidification of that droplet. Since nucleation is the rate limiting step in the solidification of an undercooled liquid, the onset of exothermic crystallization in a differential thermal analysis (DTA) record represents the nucleation temperature. In addition, a fine droplet sample is well suited for phase identification analysis by x-ray diffraction.

III. Summary of Research Findings and Conclusions

The results of the current studies on droplet samples are of value in identifying some of the key factors governing solidification at high undercooling and emphasize the importance of nucleation in determining the

nature and distribution of phases following rapid solidification. The
significance and implications of the observations are indicated in terms of
the phase selection process and the development of microstructural
morphology. A consideration of the results not only demonstrates the unique
potential of the droplet technique, but also provides a background for the
further development of the application of the droplet technique to the
solidification of undercooled liquid alloys. For most of the observations
that are given in the following presentation a more detailed discussion along
with a full description of data has been given in progress reports which have
been submitted previously and in literature publications. In addition, it is
worthwhile to note that although the results that are presented involve
observations on specific systems, many of the findings have a general
validity.

1. As an initial step in alloy solidification studies the droplet
    emulsion technique has been applied to examine the maximum
    undercooling behavior for a number of pure metals. As noted in
    previous reports large undercooling values have been obtained for
    several pure metals such as Pb, Sn, In and Bi which exceed those
    obtained in past studies by substantial amounts in some cases.[3-7]
    A further improvement in maximum undercooling has been obtained in
    the present work and several new metals have been examined in droplet
    form. A summary of the present results and a comparison with the
    undercooling values reported in past studies are presented in the
    list given in Table 1. At present the increases in observable
    undercooling are not uniform in each case. They do indicate,
    however, that the undercooling limit of 0.2 T_m (where T_m is the
    absolute melting temperature) which is quoted often should not be

regarded as a firm limit. This implies that similar large increases in maximum undercooling can be observed for other metals. In addition to providing a basis for the study of alloy solidification, the increased maximum undercooling values indicate a need to reconsider the estimates of σ_{LS}, the liquid-solid interfacial energy. An estimated value for σ_{LS} may be calculated from classical nucleation theory and the maximum undercooling.[3] This calculation implies that the present undercooling limits require an increase of up to 50% in the value of σ_{LS} estimated from nucleation theory.

2. The high kinetic resistance of liquids to crystallization when free from relatively active nucleants that has been observed in pure components is also possible in alloys. The large undercoolings that have been obtained for pure metals may be maintained in alloy droplets. In general there appears to be a trend in alloys for the maximum undercooling nucleation temperature, T_n, to follow approximately the composition dependence of the liquid phase boundary. When competing reactions are detected in the determination of T_n and phase selection at maximum undercooling this general trend may not be followed.[2] Another important exception to the T_n trend has been observed in Al-Fe alloys. As noted in Table 1 for the Al-5 w/o Fe alloy[8] $\Delta T = 260°C$ while $\Delta T \approx 160°C$ for pure Al. The origin of this behavior may be related to a modification of the Al_2O_3 coating that is usually present on Al droplets by an interaction with solute. This suggestion is being investigated more thoroughly in a current exploratory research effort under ARO sponsorship.

3. Each metal or alloy system often requires specific handling and treatment during the preparation of droplet dispersions. However, on

the basis of the experience developed in the current studies, a number of requirements may be given to optimize the undercooling behavior. For example, the use of high purity samples is helpful but does not seem to be mandatory. Of great importance is the generation of a droplet sample with a fine and narrowly distributed size characteristic. Another important requirement involves the use of surfactant treatments that tend to promote the formation of thin non-crystalline surface films that provide effective wetting for the liquid and poor catalysis for crystalline solid phases.

4. Further details concerning droplet size effects have been determined by examining the influence of the nature of particle size distribution on potential nucleant isolation and undercooling behavior. This required the study of individual droplet behavior which is difficult in metals. As a result a glass forming salt, $ZnCl_2$ was identified as suitable and a method was developed for determining the difference between glass and crystalline structures by an optical technique applied on an individual droplet basis.[9] During the shearing operation that is used to produce droplets it has been found that a log-normal size distribution is produced in all cases. The effect of droplet size on the glass-crystalline phase selection transition was not found to be sharp. Instead, the fraction of the droplet population at each size that was completely glass was observed to obey very closely a Poisson distribution and to the distributed over the droplet size range. Furthermore, the distribution function parameters agreed with a model in which the nucleation catalyst density is proportional to the droplet surface

area. From this separate study it is possible to understand that two different droplets of the same size can solidify to different phases due to the breadth of the phase selection transition in terms of droplet size.

5. An important operational parameter in rapid solidification processing is the applied cooling rate. The effect of cooling rate on T_n is usually thought to be small due to the relatively sharp onset of nucleation in an undercooled liquid. A closer inspection of the nucleation kinetics and an analysis of the rate expressions appropriate for solidification of undercooled droplets has been completed for continuous cooling conditions.[10] Both the influence of competition between different phase selection reactions and the distribution of catalysis sites on nucleation were examined for droplets. Several features of the crystallization behavior were clarified and have been discussed in detail in literature reports.[2,10] For illustration two highlights of the analysis can be noted in the context of the present discussion. First the sensitivity of the nucleation temperature to cooling rate can be related to the kinetic barrier to nucleation and the level of catalytic potency. Relatively easy (i.e. low kinetic barrier) nucleation is associated with a high catalytic potency and a significant increase in undercooling with increasing cooling rate. With catalysts of potency $C_1 > C_2$ in a droplet sample, an increasing cooling rate can shift the nucleation kinetics from control by C_1 to control by C_2, but further increase in cooling rate will yield a decrease in the incremental gain in undercooling. As a consequence, the expansion of phase selection possibilities due to a continued

increase in cooling rate is a diminishing benefit. In addition, the kinetics analysis has identified catalytic site density as an important parameter. If there are catalysts of potency $C_1 > C_2$, but the density of C_2 exceeds that of C_1 then a transition from a metastable phase product controlled by C_1 to an equilibrium product controlled by C_2 is possible with increasing cooling rate. This possibility has received experimental support in two separate alloy systems in droplet experiments.[11a-b] Under such conditions of nucleation catalysis it is also important to recognize that instead of augmenting the yield of a metastable product phase an increase in cooling rate will yield a transition to an equilibrium phase product.

6. Several aspects of microstructural evolution during rapid solidification of liquid alloy droplets have been examined at controlled levels of undercooling. The amount of undercooling can be controlled by the use of a variety of droplet surface coatings with different catalytic potencies. One study has been focussed on the Bi-Sb system which is characterized by a continuous series of solid solutions. In this system the initial solidification product following nucleation is a region of uniform composition. Subsequently, during rapid crystal growth, recalescence will increase the droplet temperature. If the reheating causes the temperature to exceed the solidus, a segregation pattern will develop in the final microstructure. The maximum recalescence temperature, T_r, and the extent of solute segregation is dependent upon the undercooling at the onset of nucleation. X-ray diffraction lattice parameter measurements have confirmed the presence of a segregation pattern and have provided a means of setting a limit on the extent of segregation

in terms of composition range. This limit in turn can be used

estimate the recalescence temperature by means of the pl

diagram. Specific thermal cycling DTA measurements have |

developed to provide additional confirmation of the recalesc

characteristics. Since the solute profile is effectively frozen

the onset of melting during heating provides a measure of one 1

to the extent of segregation and the final droplet mel1

temperature yields another limit as well as a measure of the max

recalescence temperature. This approach allows for the establishm

of a temperature pair between T_r and T_n or ΔT and the extension

this relationship to obtain the ΔT value at which T_r equals the a

solidus. At this point the ΔT value reprsents the onset

hypercooling where isenthalpic solidification is possible.[1]

results for several alloy compositions in the Bi-Sb system indica

fairly close agreement (i.e. within 5%) between the undercoo

value determined experimentally for the onset of hypercooling and

value calculated from an adiabatic solidification model.

agreement represents an important confirmation that essenti

adiabatic conditions hold during rapid solidification.

7. The solidification behavior of undercooled liquid droplets in sev

eutectic alloy systems has also been studied in the investigatior

microstructural evolution during rapid solidification. Ag

alternate nucleation sites that are generated by the applicatior

different surfactant treatments have been used to produce contro

undercooling levels. Several interesting microstructural transit

have been documents in Pb-Sb alloys.[12]

An example of uniform undercooling to a single crystallization exotherm is represented in figure 1 for a Pb-11.4 a/o Sb alloy. The nucleation onset occurs at T_n = 113°C which is equivalent to a ΔT of 162°C below the alloy liquidus, T_L. The sensitivity of the undercooling behavior to alternate nucleation sites is also illustrated in figure 1 where the cooling trace yielding final crystallization at T_{HET} (185°C) represents the catalysis of an α-Pb primary phase in promoting solidification. A summary of the undercooling behavior of Pb-Sb alloys for compositions spanning the eutectic is superimposed on the portion of the phase diagram plotted in figure 2.

The apparently simple behavior of the undercooling trends reported in figure 2 however, does not reflect the variety of microstructural patterns developed in droplets following rapid solidification. This variety is illustrated for a Pb-14.4 a/o Sb alloy by the microstructures given in figure 3. At a low ΔT of 14°C the microstructure in figure 3a reveals coarse α dendrites with a complex regular eutectic within interdendritic regions and would be representative of a conventional processing treatment. In droplet samples at an undercooling level of 111°C a strongly, modified microstructure is evident in figure 3b. In this case the light, clear regions represent an α primary solid solution which was supersaturated up to the alloy solute content while the remaining region represents a fine scale two-phase mixture. The initial supersaturation of the α phase has been established by separate x-ray diffraction (XRD) measurements on droplet samples immediately following thermal analysis. During sample preparation to reveal

interior droplet sections, the superaturated α phase undergoes a precipitation reaction which produces a pattern of fine, dark Sb precipitates. Another stage of microstructure modification is apparent in the micrograph of figure 3c corresponding to droplet solidification at a ΔT of 162°C. In this case, XRD measurements have been used to establish that the initial solidification structure was supersatured α phase which decomposed during sample preparation to yield a fine scale precipitation of the Sb phase.

Based upon the measured undercooling values and the initial droplet structures, it is possible to develop an understanding of the observed microstructure modifications in terms of an adiabatic solidification model. When T_n is close to T_L, a segregated structure can develop as in figure 3a. It is possible for crystallization to yield a solid of the alloy composition C_0 as T_n is reduced to below T_0 which represents the onset of partitionless solidification and ia also drawn schematically in figure 2. Since the rate of crystal growth following nucleation in a highly undercooled liquid is rapid, the latent heat will evolve at a rapid rate during recalescence. The temperature rise during recalescence reduces the amount of interfacial undercooling and the growth rate which for a solid of composition C_0 can reduce to zero upon reaching T_0 which appears to set a bound to partitionless solidification. Toward the end of recalescence and during final droplet solidification the solid composition can change leading to a segregated structure and a mixed morphology (figure 3b). With the adiabatic model, when the undercooling is sufficient so that the recalescence temperature rise does not lead to the development of solute partitioning,

solidification can occur entirely to a single phase solid as shown in figure 3c. The limiting undercooling for this process defines the onset of hypercooling, ΔT_H which is given to first order by $\Delta T_H = \Delta H_m/Cp$ where ΔH_m is the latent heat and Cp is the liquid heat capacity. In Pb-Sb alloys ΔT_H appears to be reduced with solute content from about 157°C for pure Pb to about 130°C for a Pb-14.4 a/o Sb alloy. This is in agreement with the solidification of a supersaturated solid solution in droplets at $\Delta T = 162°C$ and the formation of partially segregated droplet structures at $\Delta T = 111°C$.

In a number of hypoeutectic alloy compositions microstructural patterns similar to those reported for the Pb-14.4 a/o Sb alloy have been observed. For alloy compositions near the eutectic a different pattern of microstructure developed with increasing undercooling. A complex regular pattern developed at ΔT of 19°C. At undercoolings from 70 to 130°C the eutectic pattern is replaced by a dendritic microstructure instead of single phase α. The transition from a eutectic to a dendritic morphology with increasing undercooling has been observed to occur also in hypereutectic alloys and appears to be related to the coupled zone for eutectic growth. The coupled zone region usually tends to be skewed toward compositions rich in the facetting component such as Sb.[13] As a result with increasing undercooling, a transition can occur from a eutectic to a dendritic structure. In addition, measurements of the secondary dendrite arm spacing (DAS) reveal only a small decrease from 0.37 μ at $\Delta T = 70°C$ to 0.23 μ at $\Delta T = 130°C$ in the eutectic alloy which suggests that a significant structural coarsening may control DAS at high undercooling.[14] In this case the application of DAS measurements

to characterize parameters such as solidification rate may not be reliable.

8. In the Pb-Sn system the development of eutectic microstructure has been examined at two levels of undercooling.[15] At low undercooling a primary α-Pb solution forms at 40°C below the liquidus with a final solidification at 56°C below the eutectic. However, XRD evidence indicates that final solidification includes the catalysis of a metastable phase by α-Pb in a manner similar to that characteristic of a metastable peritectic reaction. Furthermore, in situ lattice parameter measurements suggests that the favorable catalysis of the metastable fct α_1 phase by α-Pb is related to the relatively low misfit of respective close packed planes (<5%).[11a] The relative misfit for α-Pb and β-Sn is at least 18%. Since the α-Pb phase acts as a nucleant for α_1, this result suggests that heterogeneous nucleation can play an important role in the development of microstructures based on metastable phases. At high undercooling ($\Delta T = 115$°C) solidification yields an equilibrium two-phase mixture with no evidence for a metastable phase. However, the morphology of the microstructure is irregular instead of the usual lamellar eutectic form developed in Pb-Sn alloys. Based on additional isothermal holding treatments, it appears that the two-phase irregular morphology is influenced strongly by coarsening. During rapid solidification the extremely fine scale product microstructures are susceptible to very rapid coarsening rates. Clearly, such coarsening effects must be incorporated into the interpretation of thermal history during rapid solidification based on microstructural observations.

9. Several microstructural transitions that depend on alloy composition
    and undercooling have been identified and related to reactions in the
    liquid state. During the processing of monotectic alloys large
    compositional segregation of the liquid can precede final
    solidification. Under normal treatment with bulk ingots, a coarse
    scale phase distribution is obtained as a result of convection and
    sedimentation effects. In undercooled dropletls of Bi-Ga and Cu-Pb
    alloys with compositions near the monotectic point, a relatively fine
    scale segregation has been observed for two-phase samples.[16] It is
    believed that this observation reflects a reduction in fluid flow
    forces in fine droplets. Also, near the critical point of
    miscibility gap, Bi-rich and Cu-rich alloys exhibit some undercooling
    prior to phase separation while in Ga-rich and Pb-rich alloys the
    onset of phase separation is at the miscibility gap boundary. These
    observations are consistent with the operation of a critical point
    wetting behavior[17] which can preclude the attainment of a fine-
    scale uniformly distributed microstructure even in fine droplets.

    Often it is implicity assumed in solidification that an initial alloy
    liquid is compositionally homogeneous. During conventional
    processing this feature may be assessed by examining the equilibrium
    phase diagram. However, during rapid solidification liquid
    undercoolings that are large may be encountered so that it may be
    necessary to reconsider the assumption of initial melt homogeneity.
    For example, at high undercooling the alloy liquid may enter into the
    domain of a metastable miscibility gap. The role of initial melt
    constitution on microstructural development in rapid solidification
    has been examined in the Pb-Cd system which exhibits an equilibrium

eutectic reaction.[12]   However, for hypereutectic alloys, DTA studies on undercooled droplets reveal that prior to crystallization a phase separation can occur in the liquid.   Subsequent solidification yields a microstructure consisting of a Pb-rich shell surrounding a Cd-rich spherical core which is a substantially different morphology than that developed during usual eutectic solidification.   In general the tendency for liquid demixing may be judged from a thermodynamic analysis and the slope of the liquidus. It appears that this feature can be a relatively common occurrence at large undercooling and for conditions involved in glass formation.

10. Substantial undercooling levels ($\Delta T \geq 160^{\circ}C$) have been measured by differential thermal analysis, DTA, for slowly cooled droplet emulsions of pure Al, and a number of Al-Fe and Al-Si alloys.[8,18] Droplet samples are produced by a modified emulsion technique which involves the high speed mechanical shearing of a mixture of molten metal and salt.   The observed level of undercooling of droplet samples has been examined as a function of the sample size distribution, externally applied cooling rate, melt superheating temperature and composition.   The maximum undercooling occurs in the finest droplets and appears to be limited by the catalytic influence of the droplet oxide coating.   Comparison studies have also been conducted on the undercooling response and microstructural development in selected alloys that have been prepared as droplet emulsions and by commercial air atomization.

For Al-Si alloys an examination of solidification catalysis reveals that hypereutectic alloys can sustain an undercooling, ΔT_{HET}, below the eutectic of 117°C in the presence of primary Si while the

introduction of primary Al in hypoeutectic alloys limits ΔT_{HET} to 57°C. Similar experiments Al-Fe alloys indicate that for both hypoeutectic and hypereutectic compositions, ΔT_{HET} values in excess of 90°C can occur in the presence of Al or Al_3Fe primary phases. In fact, for cooling cycles from above the liquidus, ΔT exceeds 260°C in cases where Al_3Fe formation is avoided.

In both slowly cooled droplets and rapidly quenched samples of Al-Fe alloys, the metastable Al_6Fe phase is an important microstructural constituent. The formation and thermal stability of Al_6Fe has been examined by metallography, XRD and DTA. With droplet samples the Al_6Fe phase has been retained during heating up to a metastable (Al-Al_6Fe) eutectic at 649°C. Microstructural observations reveal that both slowly cooled droplets and rapidly quenched powders exhibit a transition in morphology that reflects the thermal history of recalescence during rapid crystallization. In Al-Fe samples an optically featureless zone adjacent to the powder surface appears to develop initially and to evolve radially into a coarser $Al-Al_6Fe$ eutectic. Droplet solidification can yield a microstructure similar to that formed in atomized powder. The level of phase refinement has been observed to vary in microstructures of powder samples with a wide size distribution and an associated broad temperature range of crystallization. The microstructural variations with powder size are related to thermal history effects due not only to a changing cooling rate, but also to a modified undercooling behavior. These observations highlight the role of undercooling and indicate that the

droplet approach can be effective in examining potential advanced Al alloys and in optimizing processing procedures for rapid quenching treatments.

11. An investigation into the undercooling and nucleation behavior of metal droplet dispersions has been conducted on selected samples at pressures ranging up to 4.0 kbar. In pure Bi at the maximum undercooling of 0.41 T_m a fraction of the droplet sample crystallizes as a metastable phase. The dual nature of the solidification products are revealed by the appearance of a melting endotherm at 174°C in addition to the melting at 271°C for the stable phase. The application of pressure to the undercooled droplets promotes an increased yield of the metastable Bi(II) phase so that above 1 kbar complete solidification occurs to Bi(II). Furthermore, even in droplets which do not yield a Bi(II) product due to insufficient undercooling, the application of pressure can induce nucleation of a Bi(II) product. Since pressure levels of a few kbar will not alter the relative thermodynamic stability of Bi(I) and Bi(II) to a significant extent, it appears that pressure can have a significant influence on the relative nucleation kinetics. It is also remarkable that modest pressure levels (~ 1 kbar) can act to alter phase selection. Similar results have been obtained in Sn-65 w/o Bi alloy droplets where a pressure of less than 1 kbar has allowed for the nucleation of a metastable intermediate phase at undercooling levels that usually yield an equilibrium two-phase mixture. The resulting microstructures represent uniform single phase solids and indicate an interesting further possibility to promote partitionless solidification.

12. From an examination of nucleation in several binary eutectic alloys, two distinct reaction paths have been identified to operate during the formation of extensions of solid solubility and during the generation of metastable intermediate phases.[2] Both reaction paths originate with a droplet configuration containing a primary phase-liquid two-phase mixture. During cooling the growth of the α phase can proceed at a composition given by the metastable extension of the solidus. As long as the undercooling representing the potency of the α phase to catalyze the nucleation of the second eutectic solid, β , from the liquid is not achieved, a continued growth of α may proceed under local interfacial equilibrium. The resulting product can be entirely α phase with a composition gradient in the supersaturated portion (α_{ss}) . The magnitude of the composition gradient produced by this process depends on the rate of interdiffusion and the initial temperature for formation of the α phase catalyst during cooling below the liquidus.

Another possible phase reaction sequence has been identified for the catalysis by a primary α phase in selecting a metastable γ phase rather than the stable β phase during solidification. In this case the liquid in contact with the α phase at the nucleation temperature is undercooled by an amount ΔT_γ below the melting point of the γ phase and by ΔT_β below the β phase liquidus. The operation of the sequence $(\alpha + L) \rightarrow (\alpha + \gamma)$ requires that the catalysis of α for γ nucleation is greater than that for β nucleation by an amount that can compensate for the reduced driving free energy available for γ formation compared with β nucleation. A number of examples consistent with the operation of both of these

solidification paths have been demonstrated, including cases where crystalline-amorphous two-phase mixtures can form at high undercooling.

Based on the results from a number of alloy systems and solidification reactions, an analysis is being formulated for the competitive solidification kinetics that can operate in undercooled liquids. One of the central objectives in this work which is continuing is to identify the key factors involved in controlling the phase selection process. For example, it is apparent during RSP that the nucleation and/or growth of a stable phase may be difficult. In this case, the liquidus, solidus or other thermodynamic data for a metastable phase are important for the interpretation and prediction of the phases present. Various techniques have been developed to obtain information about metastable equilibrium from measured stable equilibrium data.[19] Extrapolations of phase boundaries as functions of temperature, pressure or composition into regions of metastability can be constructed directly on the equilibrium diagram to reveal the possible product phase selection. These constructions can be performed more quantitatively with analytical methods using thermodynamic modelling of the free energy function consistent with measured data. Further work on a coupling of metastable phase diagrams with a kinetics analysis is in progress and can contribute to an effective alloy design and processing during rapid solidification.
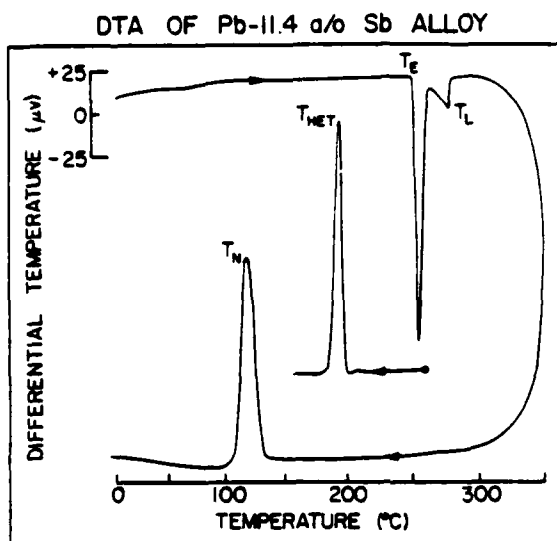
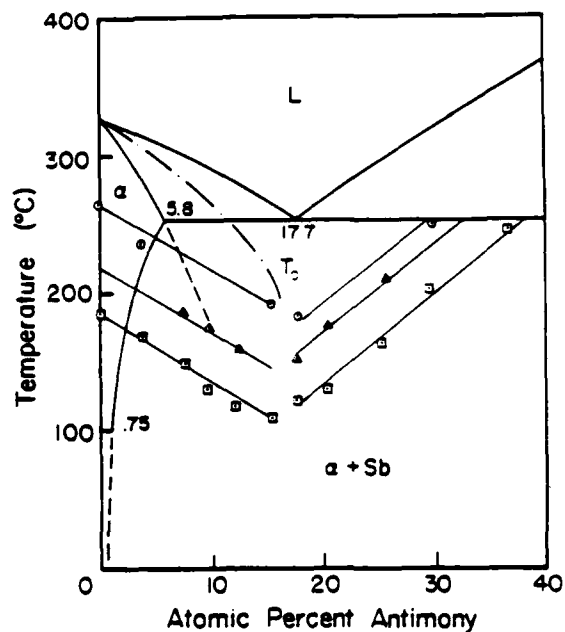Fig. 1 DTA Thermogram for Pb-11.4 a/o Sb alloy droplets.

Fig. 2. Summary of undercooling behavior in Pb-Sb alloys. Different symbols refer to undercooling trends produced by different droplet surface coating treatments.
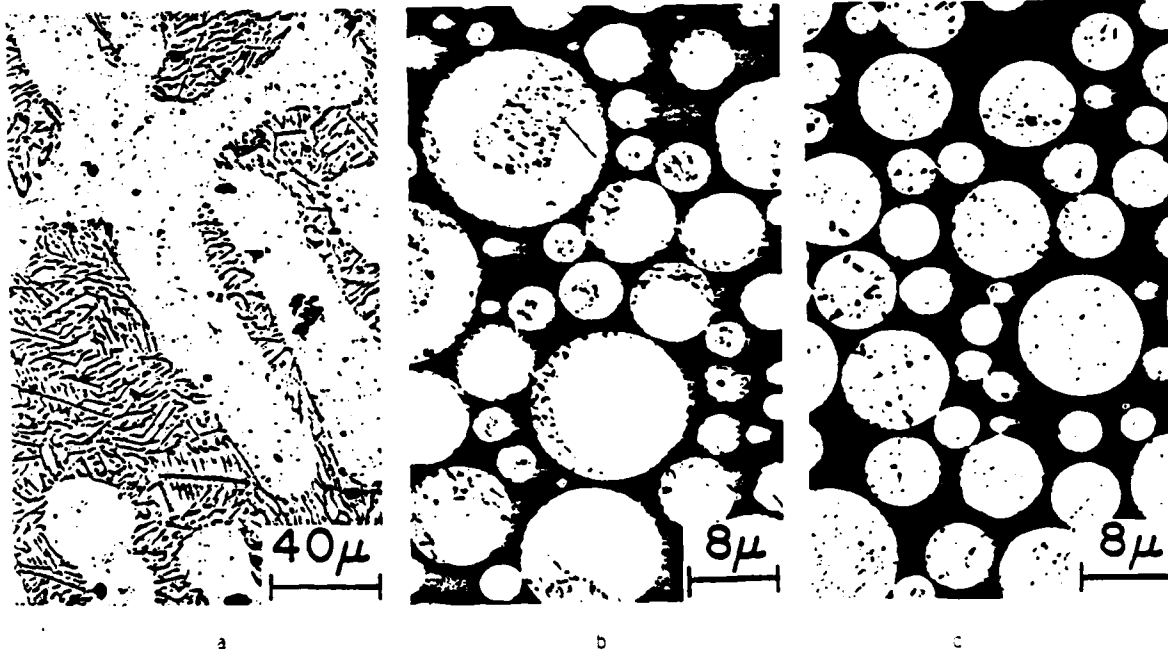

Fig. 3. Solidification microstructures developed in Pb-14.4 a/o Sb alloys at different undercooling levels (a) $\Delta T = 14°C$; (b) $\Delta T = 111°C$; (c) $\Delta T = 162°C$.

TABLE I

Maximum Undercooling Limits

Material	Previous Studies			Current Studies	
	$\Delta T(^{\circ}C)$	$\Delta T/T_m$	Ref.	$\Delta T(^{\circ}C)$	$\Delta T/T_m$
Al	130	0.14	4	160	0.17
Al-5 w/o Fe	----	----	----	260	0.26
Sb	135	0.15	4	210	0.23
Bi	90	0.16	4	227	0.41
Cd	----	----	----	110	0.19
Ga	150	0.50	6	174	0.58
In	----	----	----	110	0.26
Pb	80	0.13	4	153	0.26
Hg	80	0.34	5	88	0.38
Te	----	----	----	236	0.32
Sn	117	0.23	7	187	0.37

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Publications of the Current Research Program

During a research program, substantial time intervals often e
between the completion of a research study, submission of a manuscript an
final appearance of a paper in print. As a result, the following list
publications in preparation. As well as those in print or in press.

1. "Metastable Phase Formation in Undercooling Liquids" J. H. Pere
    and I. E. Anderson in Synthesis and Properties of Metastable Ph
    Edited by T. J. Rowland and E. S. Machlin, TMS-AIME, Warrendale
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2. "Glass Formation and Crystallization in Highly Undercooled
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3. "Crystallization of Undercooled Pb-Sn Alloys", K. P. Cooper, I. E. Anderson and J. H. Perepezko in Proceedings of the 4th Int. Conf. on Rapidly Quenched Metals (The Japan Inst. Metals, Sendai) vol. 1 107 (1981).

4. "Synthesis of Non-Equilibrium Structures in Undercooled Liquid Droplets", J. H. Perepezko and J. S. Paik, Proceedings of the 29th Midwest Solid State Conference: Novel Materials and Techniques in Condensed Matter, Eds. G. Crabtree and P. Vashishta (North Holland, NY) p. 57 (1982).

5. "Solidification of Undercooled Monotectic Alloys", J. H. Perepezko, C. Galaup and K. P. Cooper, Mat. Res. Soc. Symp. vol. 9: Materials Processing in the Reduced Gravity Environment of Space, (North Holland, NY) p. 491 (1982).

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10. "Solidification Microstructures of Undercooled Droplets", J. J. Richmond, J. H. Perepezko, S. E. LeBeau and K. P. Cooper in "Rapid Solidification Processing: Principles and Technologies III" Ed. R.

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12. "Nucleation in Undercooled Liquids", J. H. Perepezko, Mat. Sci and Eng. (in press).

13. "Rapid Solidification of Highly Undercooled Aluminum Powders", J. H. Perepezko, S. E. LeBeau, B. A. Mueller and G. J. Hildeman, ASTM special publication: Rapidly Solidified Al Alloy Powders (accepted for publication).

14. "Crystallization Kinetics in Undercooled Droplets" J. H. Perepezko, B. A. Mueller, J. J. Richmond and K. P. Cooper, submitted for Proc. RQ-5 Conference, Würzburg, Germany (1984).

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Patents

U.S. Patent No. 4,321,086 - Metal Droplet

Formation of High Melting Point Metals

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